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Method of producing stable thin-film resistant material

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DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a method of producing a stable thin-film resistant material obtained by applying a principle of silver complex salt diffusion transfer method which is one of the photographic reproducing methods.

In the preparation method of the thin-film resistant material of the present invention, the conventional coating method, the vacuum deposition method, etc., can be utilized as a part thereof. However, at the final stage, a novel diffusion transfer system which has never been utilized in this field is used, and light-sensitivity of a silver halide emulsion for photography can be effectively utilized so that a body structure of a thin-film resistance can be formed extremely freely, precisely, finely and with good reproducibility. Thus, it is convenient for making a fine sized and compact sized circuit in recent electronic devices, and there are main advantages that resolution at the fine part of the shape is close to that of silver halide emulsion layer to give a material of 50

lines/mm, it can obtain a stable thickness of several hundreds Å even when it is a significantly higher resistant value, and a uniform resistant film material with a free shape and size and without any fluctuation in the resistance value at the lateral direction and the longitudinal direction can be obtained if a suitable manufacturing device is selected. Accordingly, the product obtained by the method of the present invention can be used not only for uniform resistant material with various kinds of uses but also can provide a resistance element conductive material extremely simple and easy, and industrially advantageously for the constitution of ultra-small sized circuit (for example, micromodule electronics, etc.) which has been employed a complex method at the present stage. Also, according to the method of production of the present invention, a range of limitation in the respective steps of the production process for securing the quality of the resulting material is significantly wide so that an error is a little and stable, and yet reproducibility is also good so that it is suitable for mass production. Moreover, when the product according to the present invention is used, since a thin film resistance circuit having an optional pattern can be obtained by a usual photographic printing operation so that it can be obtained easily with a cheap price for development of a novel industrial material.

For the production of the resistant material according to the present invention, a silver halide emulsion layer which comprises a supplying source of a soluble silver salt, a resistant material support layer which receives the above layer by transfer and becomes a positive layer containing nuclei of a heavy metal or a compound thereof which becomes a support for formation of reduced silver, and a developing solution for diffusion transfer are necessary. As a usual resistance material which does not require specific electric characteristics, those of a commercially available light-sensitive material for copying at present can be diverted with regard to a silver halide emulsion layer and a developing solution, and only a fine particle layer of a heavy metal or a compound thereof which becomes a nucleus of a silver salt reduction formed on an insulating material which finally

becomes a support of a resistant material is to be specifically prepared. At present, a silver complex salt diffusion transfer method utilized as photographically (this principle is described in the specifications of U.S. Patent No. 2,352,014 and German Patent No. 887733), and a colloid layer containing nuclei of heavy metallic, i.e., the so-called silver image in a positive layer according to the following operation principle. That is, a photographic emulsion layer containing a light-sensitive silver halide is exposed through an original image, and this is pressed to a positive layer in the presence of a developing agent and a soluble silver complex salt-forming agent. In this case, the silver halide at the exposed portion is developed (a negative image) so that no change occurred thereafter, while an undeveloped silver halide at the unexposed portion is to be made a complex (complexion) by a soluble silver complex salt-forming agent in a developing solution to become water-soluble whereby it is diffused and transferred onto the surface of said image-receiving material. When this positive layer is peeled off from the above-mentioned silver halide emulsion layer, an (positive) image having the same shading shape as the original image is formed. The method of producing a resistant material of the present invention is basically similar to the silver complex salt diffusion transfer method in the photographic field, but a positive image receiving layer such as paper presently used, etc., simply gives a photographic positive image, and characteristics which can utilize electrically do not exist at all. The reason is that, in the positive layer which is utilized photographically, metal silver precipitated by reduction on a catalytic nucleus becomes an aggregate of insulating particles which are completely encapsulated by a protective colloid contained in the layer with a large amount such as gelatin, etc. In the present invention, to provide a suitable electric conductivity to the positive image formed on the support having electrically insulating property, the positive image-receiving layer is specifically adjusted, electron conduction is to be occurred between precipitated particles and the silver thin film is to be exposed on the surface of the support layer. In general, in the silver complex salt

diffusion transfer, reduction of silver complex salt ions is extremely activated in the presence of fine particles of a metal, or sulfide thereof, etc., and it is characterized in that growth of the reduced silver rapidly occurs using these fine particles as a core or nucleus of precipitation. In the present invention, in order to produce a silver thin film which can be the above-mentioned resistant material, a fine particle layer such as various heavy metals or, a compound thereof, etc., is coated on a suitable resistant support as a catalytic nucleus of a transfer image (positive image) by the vacuum deposition method, cathode sputtering method, coating method, etc. Accordingly, the vacuum deposition method, coating method, etc., which is a part of the production method of the present invention is merely a means for forming a catalytic nucleus of reduction of a silver ion or a silver complex salt ion, and is not to obtain a final product. That is, the fine particles such as a heavy metal, etc., thus prepared is a complete insulating film having an insulating resistance of 1000 MΩ or higher in an electric field of 1000 V/cm. This limit corresponds to 10Å in average in a vacuum deposition film, and several mg per square meter in weight, and generally speaking, a layer with such a thickness constitutes not a continuous film but an island-like structure, and it has been known that it is an insulating material which does not pass even a tunneling current.

The amount is not changed in the case of coating a heavy metallic colloid prepared chemically, and it is required that an amount of an insulating organic colloid which becomes a binder is made as little as possible. In the present invention, diffusion transfer (reduction precipitation) of the silver complex salt is carried out on the insulating film whereby a size of the fine particle of the heavy metal or a compound thereof is made larger to contact with each other whereby a silver thin film which can be a practical film resistance is produced.

A structure of the metal silver thin film obtainable by the production process of the present invention is significantly different from a silver thin film prepared by the vacuum deposition method, etc., and has the following electric

characteristics. A silver amount of the resistant thin film obtained by using a commercially available negative material for diffusion transfer and a developing solution according to the method of the present invention is 4 to 500 mg/m^2 according to the X-ray fluorescent analysis and an electric resistance thereof is set in the range of 10 to 100 Ω/□. Further, with regard to a resistant material in the range of 100 to 100 KΩ/□ which is more than the above, a material having an optional value can be obtained by suitably changing the silver halide emulsion or a prescription of the developing solution, and controlling an exposure dose or dipping in an aqueous oxidizing solution such as sodium hypochlorite, etc. In these silver thin films, their temperature coefficient of resistances are markedly reduced by carrying out a suitable heat treatment (for example, at 100°C for 5 hours), and it can be made several PPm/°C between 0 and 100°C). In general, in a metal or alloy thin film, a thickness of the film is thick, and accordingly, when it is low resistance, its temperature coefficient of resistance is positive, but when the film is thin and becomes high resistance, it has a coefficient of 0 to at last a negative value. A thickness of the film at which the temperature coefficient of resistance becomes 0 varies depending on the compositional structure of the film, etc., and in many cases, it is said to be present between 100 and several hundreds Ω/□. However, in the case of the transfer silver film, it has a negative temperature coefficient of resistance even in the material of several tens Ω/□, and it becomes substantially 0 by a heat treatment. Incidentally, with regard to high temperature and high humidity, significant change in a resistance value can be observed, so that it is desired to coat a humidity-resistant protective film such as a phenol resin, epoxy resin and a polymer material, etc., or in an ultra-small sized circuit, a suitable insulating material such as silicon oxide, etc., is vacuum deposited or coated.

According to an electric passing test with the direct current voltage application of 1 W/cm^2 or so using a standard silver thin film obtained by the production method of the present invention, change in the resistance value in air after 100 hours is 0.01% or less. Also, as compared with the

conventional thin film resistance, frequency characteristics are extremely good, and it is prepared, for example, on a Tetron film. In a transferred silver film, the frequency characteristics do not substantially appear by the measurement using Boorton R X meter by 250 MC/S, and an impedance of 200 MC/S is the same as the direct current resistance value.

Such a production method of the transfer silver film can employ various kinds of methods depending on the uses of the obtainable films. For example, on a Tetron film on which a suitable undercoating has been applied to, silver, etc., is vacuum deposited under a reduced pressure of 10^{-3} to 10^{-6} mmHg. This deposition is to carry out that a particle with a size of 20 to 100Å or so is distributed with a distance of 10 to 100Å or so, and such a distribution is called as an island-like structure film, which structure appears at an initial stage of producing a vacuum deposition film and is extremely easily obtained. This film is taken out in an air, a silver halide emulsion film exposed through an original image is adhered thereto and it is passed through a developing solution containing a soluble silver complex salt-forming agent, whereby a silver thin film resistant pattern which is the same as the original image with a precision of ±0.05 mm or less can be obtained. Also, in a glass plate, natural mica, Bakelite, polymer film, etc., after coating catalytic nucleus, a silver halide emulsion layer which is made in a state easily peeled off with water is coated thereon, or a silver halide emulsion having suitable prescription may be coated through an intermediate layer such as a water-soluble resin, polymer, etc. In a product in which a fine particle layer of a heavy metal or a compound thereof which becomes a catalytic nucleus and a silver halide emulsion layer are subjected to multi-layer coating on one of such a support, an optional pattern of a silver thin film can be formed easily for a user. That is, depending on a prescription of the silver halide emulsion, exposure is carried out by contact or enlargement, and after an operation (it is possible with one bath) of development and transfer, the emulsion layer on the surface is flown away with running water so that all these operations can be carried out with 5 minutes or longer. Also, these operations are matters

all of which can be automated.

As described above, in the production method of the present invention, there are some stereotypes and even when either of the methods is employed, setting of electric characteristics such as a resistant value, etc., can be easily controlled within a wide range by choosing a kind, shape or size of the fine particle layer of a heavy metal or a compound thereof, a prescription of a silver halide emulsion layer, and further a prescription of a developing solution for diffusion transfer. This can never be seen in the production methods of the conventional resistant materials, and it can be considered to be one of the excellent merits of the present invention. Moreover, depending on the various uses, a treatment for changing or modifying physical or chemical properties of the film layer or the surface thereof, such as electro-deposition, burying into the insulating substance, surface coating, soldering, coloring, etc., can be carried out.

Next, Examples of the present invention are shown, but the method of the present invention is not limited by these.

Example 1

By using a small sized vacuum deposition device for an experiment, silver sulfide powder is evaporated by heating under resistance a molybdenum boat while moving a Tetron film having a width of 4 cm and a length of 10 m under a reduced pressure of $5x10^{-5}$ mmHg with a rate of 10 cm/min whereby it is deposited with an average film thickness of 10 Å or so (about 0.007 g/m^2).

This silver sulfide nucleus deposited film is taken out in the air, cut to an appropriate length, and the surface and an emulsion surface of a commercially available negative paper for diffusion transfer (for example, Mitsubishi Hishirapid PF exclusively used NL) are opposed to each other in an unexposed state. These materials are passed through a liquid in which 1% by weight of sodium thiosulfate is added to a commercially available developing solution (for example, Mitsubishi Hishirapid developing solution), then, these materials are immediately adhered, and after 2 to 3 seconds, the negative paper and the film are peeled off, the whole surface of the Tetron film is a metal silver thin film. When the suface

resistance of the silver thin film is measured by the four-point probe method, it is 21 Ω/□ which is no unevenness and uniform in the resistance values to the lateral direction and the longitudinal direction.

Also, this Tetron film attaching the silver thin film is cut by a scissor with a size of 1x3 cm, electrodes are attached to the both sides with a silver paint and a direct current voltage with 10V is applied to the electrodes, then, 160 mA of a current is flown. This is allowed to stand as such in the air and change in the current value is recorded, there is substantially no change with 159 to 160 mA or so after 100 hours.

Example 2

A negative paper for diffusion transfer is subjected to contact exposure through an original image, and the same treatment of development and transfer similar to Example 1 is carried out by using a silver sulfide nucleus deposited Tetron film of Example 1, a pattern of metal silver which is the same as the original image can be obtained on the Tetron film for several seconds, and a line with a width of 0.5 mm or less has a practically applicable conductivity.

Example 3

A silver sol is prepared according to the following prescription (% means %by weight).

Solution A:	0.2% $AgNO_3$	10 cc
	1% KBr	1 cc
	2% Formalin	10 cc
	0.03N NaOH	100 cc
Solution B:	Gelatin	3 g
	Water	100 cc

Solution A and Solution B are mixed, and after removing a salt(s), etc., by a operation of dialysis, etc., then, the total amount was made 500 cc, and the material is coated onto a glass plate with a coating amount of 100 g or so (accordingly, it is 0.004 g/m^2 as Ag). When the coated material is dried, these films are practically complete insulating films. Moreover, on the surface of the film, a usual silver chloride emulsion is coated without adding a hardener and dried.

By using an enlarging apparatus for photography, on the

dry plate, an original drawing (positive) is passed to carry out exposure, and exposed and the material is dipped in a development transfer plate. When the transfer is finished with the dipping for 2 to 3 minutes, the silver chloride emulsion layer is washed away with flowing water.

When the above-mentioned treatments are carried out, a thin-film pattern of metal silver which is the same as that of the original drawing can be formed on the glass plate. These surface resistances can be set to a suitable value (10 Ω/□ to 100 KΩ/□) by a prescription of the emulsion, an exposed amount, a prescription of the developing solution, a dipping time, etc. Incidentally, the same results can be obtained even when a metal or a sulfide, etc., is vacuum deposited in the same manner as in Example 1 in place of the silver nucleus coating by the silver sol, and a silver halide emulsion is coated thereon. In this case, soldering can be carried out for attaching an electrode.

SCOPE OF CLAIM FOR PATENT

1. A method of producing a stable thin-film resistant material which comprises suitably covering reduced silver formed by acting a silver halide emulsion layer with a soluble silver complex salt-forming agent and a reducing agent on a fine particulate layer of a heavy metal which becomes a core of silver salt reduction or a compound thereof formed on an optional insulating material, whereby an electron-conductive thin film basically comprising metal silver is formed.

2. The method of producing a stable thin-film resistant material according to Claim 1, wherein a resister or an ultra-small sized resistant component having a complicated and fine structural pattern, without processing an insulating material, by optically printing an optional-shaped pattern previously to a silver halide emulsion layer which has not yet been light-exposed.